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ABSTRACT

This paper reports a study on the purification behavior of methyl isobutyl ketone (MIBK) for the major impurities of the phosphoric acid wet process (Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, SO_4^{2-}, and F^-). Distribution coefficients of phosphoric acid (PA) and impurities, as well as selectivity of MIBK for PA, have been studied as a function of the PA concentration (wt%) in the organic phase. Our results are compared to those obtained with other solvents (isoamyl alcohol, dibutyl ether, and dipropyl ether) described in the literature. MIBK seems to have the best selectivity for PA against SO_4^{2-}, and it shows an intermediate behavior between those of isomyl alcohol and ethers with regard to metallic impurities.

INTRODUCTION

Wet process phosphoric acid (WPA) contains a number of organic and inorganic impurities which impart undesirable color and affect the grade of the acid. Traditionally, furnace-grade phosphoric acid or chemically treated WPA was used in many industrial fields such as making nonsludging phosphatic solutions for liquid fertilizers, sodium tripolyphosphate for detergents, metal treatment products, and animal food additives. Recently, an increasing proportion of such needs have been met by WPA purified by solvent extraction (1–4).

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In connection with our studies on WPA purification (5, 6), the liquid–liquid extraction technique has been used in order to obtain a highly purified phosphoric acid. For this purpose, methyl isobutyl ketone (MIBK) has been used as an extractant.

In a previous paper (7) we reported solubility and liquid–liquid phase equilibrium data for the ternary system water (W)–phosphoric acid (PA)–methyl isobutyl ketone (MIBK) at 25 and 40°C. The results were compared with those corresponding to other ketones described in the literature. The aim of the present work was to carry out a systematic study at 25°C on the distribution of impurities (Ca, Mg, Al, Fe, SO_4^{2-}, and F^-) between the conjugated phases obtained when WPA (from Tunisian rock) is mixed with MIBK. The purification behavior of MIBK is compared to those of other solvents described in the literature (8–11).

EXPERIMENTAL
Raw Materials

The WPA used in this work was prepared by treating Tunisian phosphate rock with sulfuric acid. Before carrying out the extraction experiments, the dark crude acid was partially defluorinated with bentonite (12) and then treated with activated carbon (supplied by NORIT) in order to reduce its humic matter content.* The composition (wt%) of the resulting green acid was as follows:

P_2O_5	54.6% (75.3% as H_3PO_4)
CaO	0.15%
MgO ·	1.09%
Al_2O_3	0.86%
Fe_2O_3	0.48%
SO_4^{2-}	1.03%
F^-	0.048%
C	300 ppm (humic matter)

MIBK (p.a. grade) with a purity higher than 99 wt% was supplied by Fluka. Its water content, determined by the Karl-Fisher method, was 0.03 wt%.

Procedure

In order to study systematically the impurity distribution between the conjugated phases, suitable initial mixtures were prepared by adding distilled water and MIBK to the above-described green acid. Table 1 shows the composition

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* This treatment is used to prevent crude formation during solvent extraction experiments.

TABLE 1

Initial Mixtures Used for the Determination of the Impurity Distribution

	Initial aqueous phase composition (wt%)							MIBK[a]
Exp.	PA	CaO	MgO	Al_2O_3	Fe_2O_3	SO_4^{2-}	F^-	Acid
1	49.5	0.098	0.72	0.57	0.32	0.68	0.032	1
2	53.1	0.106	0.77	0.61	0.34	0.73	0.034	0.9
3	56.7	0.113	0.82	0.65	0.36	0.78	0.036	0.8
4	60.2	0.120	0.87	0.69	0.38	0.82	0.038	0.7
5	63.8	0.127	0.92	0.73	0.41	0.87	0.041	0.6
6	67.3	0.134	0.97	0.77	0.43	0.92	0.043	0.5
7	70.8	0.141	1.02	0.81	0.45	0.97	0.045	0.4
8	73.7	0.147	1.07	0.84	0.47	1.01	0.047	0.3
9	75.3	0.150	1.09	0.86	0.48	1.03	0.048	0.25

[a] Weight ratio of MIBK/aqueous phase.

of the initial aqueous phases and the weight ratios of the MIBK/aqueous phase used.

To avoid matter loss due to liquid pouring, each initial heterogeneous mixture was directly prepared in a weighed separatory funnel. The mixture was vigorously shaken for 20 minutes to achieve equilibrium and then allowed to settle for 1 hour. The conjugated phases were separated, and samples from each phase were taken for PA and impurity analysis.

Experiments were performed under thermostatic conditions at $25 \pm 0.2°C$.

Analysis

PA was determined by gravimetry using the phosphomolybdate quinoleol method (13).

Sulfate ions were analyzed by HPLC in Shimadzu HIC-6A equipment using a Shimadzu Shim-Pack IC-A1 anion-exchange column. An aqueous solution of pH 4, containing 2.5 mmol·L^{-1} phthalic acid and 2.4 mmol·L^{-1} Tris (hydroxylmethyl) aminomethane was used as an elutrient. The chromatographic parameters used were: column temperature 40°C, pressure 120 Kg$_f$·cm^{-2}, elutrient flow rate 1.5 mL·min^{-1}, conductivity detector gain 1 μS·cm^{-1}, and sample injected 20 μL.

Fluoride ions were determined by a selective electrode (Ingold) using the method of successive standard additions. TISAB IV (an aqueous solution of pH 5.3 containing 58 g NaCl, 57 mL acetic acid, 5 g CDTA, and 35 g NaOH per liter) was used to adjust the pH and the ionic strength of both samples and standard solutions (14).

Ca, Mg, Al, and Fe were analyzed by atomic absorption using a Hitachi Z-6100 spectrophotometer at λ = 422.7, 285.2, 309.3, and 248.3 nm respec-

tively. Analyses were performed in the presence of lanthane as a spectral buffer. The results are expressed in terms of the associated oxides of these metals.

The determination of the amounts of conjugated phases permitted us to carry out the material balances for the components analyzed. Average deviations obtained were 0.6% for PA, 2.3% for the metallic impurities, 2% for sulfate ions, and 3% for F^-.

Humic matter in the WPA was evaluated by the total organic carbon (TOC) method in a Shimadzu TOC 500 apparatus fitted with an IR detector (λ = 4300 nm).

Water in MIBK was determined by the Karl-Fisher method (15) using a Metrohm E551 Karl-Fisher titrator.

RESULTS AND DISCUSSION

Concentrations of PA and impurities are expressed in weight percent and symbolized by (X_i) φ, where i stands for the component analyzed (PA, CaO, MgO, Al_2O_3, Fe_2O_3, SO_4^{2-}, F^-) and φ for the nature of the phase considered ("aq" for the aqueous phase and "org" for the organic one). Tables 2A and 2B indicate the composition of the conjugated phases corresponding to the heterogeneous mixtures described in Table 1.

To evaluate quantitatively the extraction power of MIBK for both PA and impurities, we calculate—from results in Tables 2A and 2B—the distribution coefficient D_i given for each component i (PA or impurity) by the expression

$$D_i = \frac{(X_i)_{\text{org}}}{(X_i)_{\text{aq}}}$$

and the selectivity β_i of MIBK for PA against each impurity i, as follows:

$$\beta_i = DPA/D_i$$

TABLE 2A
PA, SO_4^{2-}, and F^- Composition (wt%) in Both Aqueous and Organic Phases

Exp.	$(XPA)_{aq}$	$(XPA)_{org}$	$(XSO_4^{2-})_{aq}$	$(XSO_4^{2-})_{org}$	$(XF^-)_{aq}$	$(XF^-)_{org}$
1	49.8	0.7	0.69	0.0013	0.0234	0.0090
2	52.9	1.5	0.74	0.0022	0.0242	0.0113˙
3	55.7	3.7	0.80	0.0068	0.0254	0.0138
4	57.3	10.1	0.87	0.038	0.0251	0.0192
5	60.2	18.7	0.97	0.102	0.0319	0.0191
6	62.8	28.2	1.10	0.160	0.0402	0.0179
7	65.9	37.0	1.21	0.231	0.0520	0.0145
8	68.8	45.2	1.26	0.313	0.0581	0.0153
9	70.7	50.0	1.28	0.370	0.0616	0.0153

TABLE 2B
CaO, MgO, Al_2O_3, and Fe_2O_3 Composition (wt%) in Both Aqueous and Organic Phases

Exp.	$(XCaO)_{aq}$	$(XCaO)_{org}$	$(XMgO)_{aq}$	$(XMgO)_{org}$	$(XAl_2O_3)_{aq}$	$(XAl_2O_3)_{org}$	$(XFe_2O_3)_{aq}$	$(XFe_2O_3)_{org}$
1	0.100	—[a]	0.73	0.0005	0.58	0.0008	0.33	0.0010
2	0.108	—[a]	0.78	0.0007	0.62	0.0007	0.35	0.0009
3	0.118	—[a]	0.85	0.0014	0.67	0.001	0.37	0.0014
4	0.132	—[a]	0.95	0.0029	0.76	0.0041	0.41	0.0041
5	0.155	—[a]	1.12	0.0092	0.89	0.0097	0.49	0.010
6	0.183	0.0015	1.32	0.023	1.04	0.024	0.57	0.021
7	0.212	0.0024	1.49	0.056	1.17	0.055	0.64	0.040
8	0.229	0.0031	1.57	0.104	1.22	0.104	0.67	0.066
9	0.237	0.0035	1.63	0.115	1.23	0.150	0.68	0.087

[a] Concentration below the detection limit.

The variation of D_i and β_i is studied as a function of the PA weight percent in the organic phase.

Figure 1 shows the PA distribution curves at 25°C for both WPA (this work) and pure acid (7). Despite the difference between the extraction temperatures, these results are in good agreement with those reported at 35°C by Parameswaran et al. (16) (Fig. 1) for the system H_2O–PA–MIBK. As can be seen, regardless of the quality of the phosphoric acid used, MIBK is an effective extractant for PA only with aqueous solutions containing more than
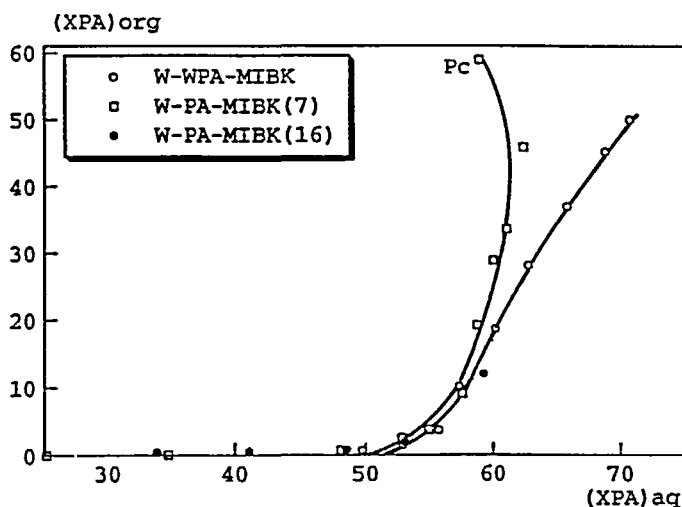

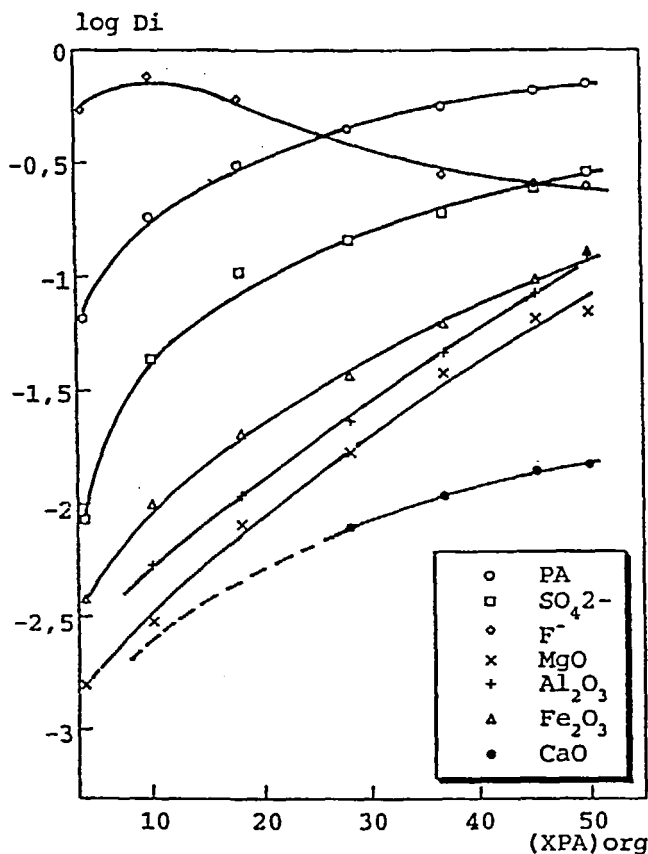FIG. 1   PA distribution curves. Pc = critical point.

FIG. 2　PA, CaO, MgO, Al_2O_3, Fe_2O_3, SO_4^{2-}, and F^- distribution coefficient for the system W–WPA–MIBK at 25°C.

50 wt% PA. On the other hand, the inorganic impurities of WPA have a negative effect on the transfer of PA to the organic phase. This effect is better marked as PA concentration (and consequently that of impurities) in the aqueous phase increases.

　　Figure 2 shows the distribution coefficient for PA and each impurity versus the PA concentration in the organic phase. Figure 3 relates the selectivity of MIBK for PA against CaO, MgO, Al_2O_3, Fe_2O_3, SO_4^{2-}, and F^-. It can be clearly seen from Fig. 3 that MIBK presents on the whole a good purification behavior for metallic impurities (high β_i values), but unsuitable for anionic impurities purification—especially F^-—due to its high anion coextraction

capacity. Moreover, and as shown in Fig. 2, metallic impurities and SO_4^{2-} follow practically the same trend, whereas F^- seems to behave differently. Indeed, the distribution coefficients of CaO, MgO, Fe_2O_3, Al_2O_3, and SO_4^{2-} increase as the PA concentration in the organic phase increases, whereas that of F^- reaches a maximum at approximately 10%. It can also be noticed that F^- is more extracted than PA when the concentration of the latter in the organic phase does not exceed approximately 28%. This particular behavior of F^- has also been observed by Marcilla et al. (11) with another ketone, namely 3-pentanone (DEK).

With respect to SO_4^{2-}, the selectivity of MIBK for PA (Fig. 3) decreases clearly for $(XPA)_{org} < 10\%$ and remains nearly constant beyond this range. On the other hand, SO_4^{2-} is extracted to a higher extent than metallic impurities in the whole $(XPA)_{org}$ range studied.
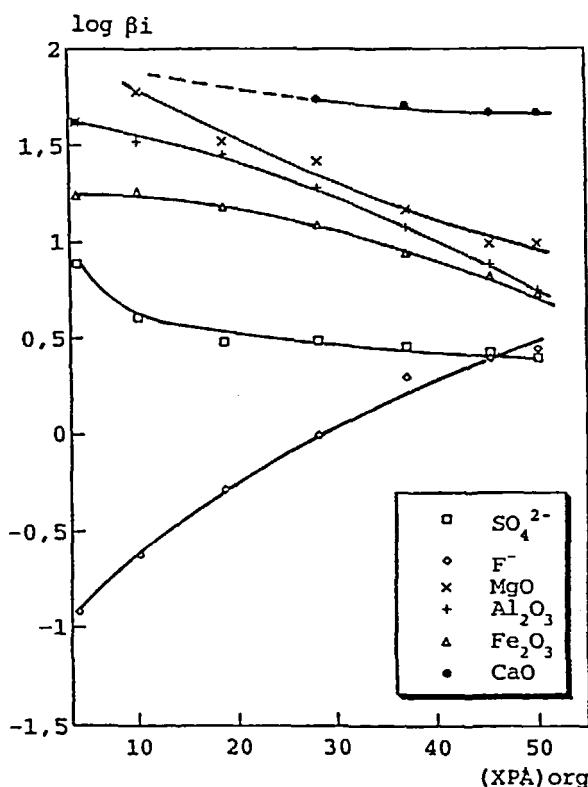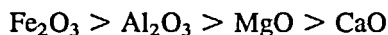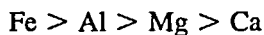

FIG. 3   CaO, MgO, Al_2O_3, Fe_2O_3, SO_4^{2-}, and F^- selectivities vs $(XPA)_{org}$ for the system W–WPA–MIBK at 25°C.

With regard to the metallic impurities, the extraction power of MIBK decreases in the order

$$Fe_2O_3 > Al_2O_3 > MgO > CaO$$

This order is related to the solvation ability of MIBK of the neutral extracted metallic species (17) which decreases as follows:

$$Fe > Al > Mg > Ca$$

It is important to note that this order also follows the general tendency of metallic ions to complexation-solvation which normally increases with charge density of the cation. The fact that $Fe^{3+} > Al^{3+}$ could be related to the former being a transition metal [ionic radii Fe^{3+} (0.67 Å) bigger than that of Al^{3+} (0.57 Å)] (17).

Finally, regardless of the specific behavior of each impurity, it can be concluded from Figs. 2 and 3 that the organic phase extracts relatively less metallic impurities and SO_4^{2-} when decreasing its PA concentration. Thus, to reextract (with water) a more purified phosphoric acid, we have to work at a low PA concentration in the organic phase. In order to illustrate this purpose, we have calculated the composition of acids recovered from extracts corresponding to Experiments 4 to 7 of Table 1. The amounts of impurities in these acids in relation to the same PA concentration of the raw acid (75.3% PA) are given in Table 3.

As indicated above, it can be seen—from the results in Table 3—that the extracted acid is relatively more purified with respect to SO_4^{2-}, and especially metallic impurities, as the PA concentration decreases in the organic phase. Moreover, it can be observed that the recovered acids have already reached a relatively high level of purity when compared to the raw acid. However,

TABLE 3
Composition of the Acids Recovered from Different Extracts

(XPA)[a] in the extract	Composition (ppm) of the recovered acids					
	CaO	MgO	Al_2O_3	Fe_2O_3	SO_4^{2-}	F^-
10.1	—	210	300	300	2,830	1,440
18.7	—	370	390	400	4,100	770
28.2	40	620	640	560	4,280	480
37	48	1,140	1,120	820	4,700	290
Raw acid	1,500	10,900	8,600	4,800	10,300	480

[a] In wt%.

they are still far from furnace-grade acid which contains less than 100 ppm of total impurities with respect to P_2O_5 (4). Thus, these stripped acids can be used as such for the preparation of low quality products like liquid fertilizers. For detergents, food, and technical-grade acids, the crude organic phase has to undergo a scrubbing step and possibly a chemical posttreatment in order to reduce still further the amount of coextracted impurities.

COMPARISON OF MIBK TO OTHER SOLVENTS

Several works dealing with the distribution of impurities between the conjugated phases generated by the system WPA/organic solvents are described in the literature. The solvents used are alcohols (8, 18–20), ethers (9, 10), and ketones (11, 19). Nevertheless, only Ruiz et al. have reported systematic studies on the distribution of impurities (Mg, Al, Fe, SO_4^{2-}, and F^-) between WPA and different solvents (8–11). In this paper the behavior of MIBK is compared to that of three other solvents, namely: isoamyl alcohol (iA) (8), dipropyl ether containing 6.4 wt% of the isomer propyl isopropyl ether [DPE(M)] (9), and dibutyl ether (DBE) (10). For this purpose we define—as did Marcilla et al. (10)—the percentage extracted of component i in the organic phases as follows:

$$\%E(i) = \frac{(X_i)_{\text{org}}}{(X_i)_{\text{org}} + (X)_{\text{aq}}} \times 100$$

This parameter is directly related to the distribution coefficient D_i by the relation

$$\%E(i) = \frac{D_i}{D_i + 1} \times 100$$

which permits a comparison among the results obtained with wet process phosphoric acids having different compositions.

Figure 4 shows the PA distribution curves at 25°C for MIBK (this work), iA, DPE(M), and DBE. Figure 5(a) relates the percent of PA extracted by these different solvents versus $(XPA)_{\text{org}}$. According to Figs. 4 and 5(a), it appears that each solvent becomes an effective extractant for PA only when the PA concentration in the aqueous phase exceeds a limit which increases in the following order:
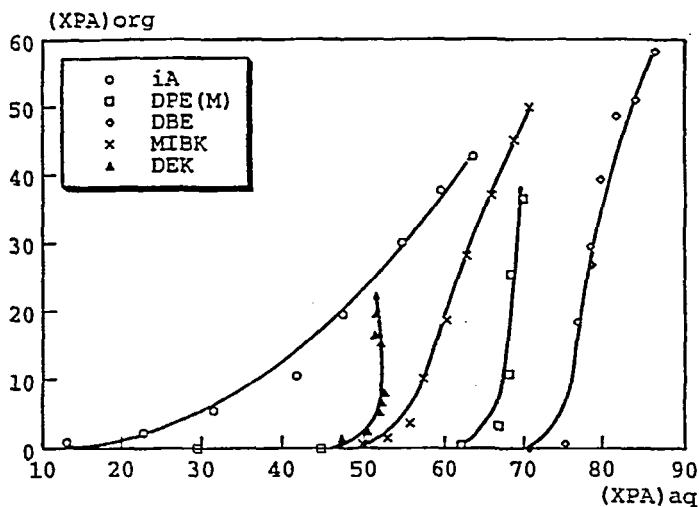
$$iA < MIBK < DPE(M) < DBE$$

FIG. 4   PA distribution curves for different solvents at 25°C.

MIBK then presents an intermediate power extraction for PA between those of iA and ethers. It can be noticed from Table 4 that the order of the extraction power does not follow exactly that of the solvent polarities (in relation to their dipole moments μ), but seems to be related to the solubility of water in the pure solvents. This observation could be considered as an interesting result since it allows prediction, as a first approximation, of the extraction power for PA of any carbon-bonded oxygen-donor solvent when only the extent of water solubility in the pure solvent is known. For example, 3-pentanone (DEK), which has a water solubility of 2.43% (23), should present an intermediate extraction power between those of iA and MIBK. The experimental data reported by Marcilla et al. (11) confirm this assertion (Fig. 4).

The shape of the PA distribution curve obtained for each solvent (Fig. 4) can be explained by considering the extraction mechanism of weak acids by solvating solvents. Indeed, the extraction of PA should be expected as a result of the competition between water and the solvent for the solvation, by hydrogen bonds, of the neutral species H_3PO_4 (24). Thus, as the PA concentration of the aqueous phase increases, the proportion of undissociated H_3PO_4 increases whereas water activity decreases (25). So the solvation of H_3PO_4 by the solvent and then its transfer to the organic phase becomes favored.

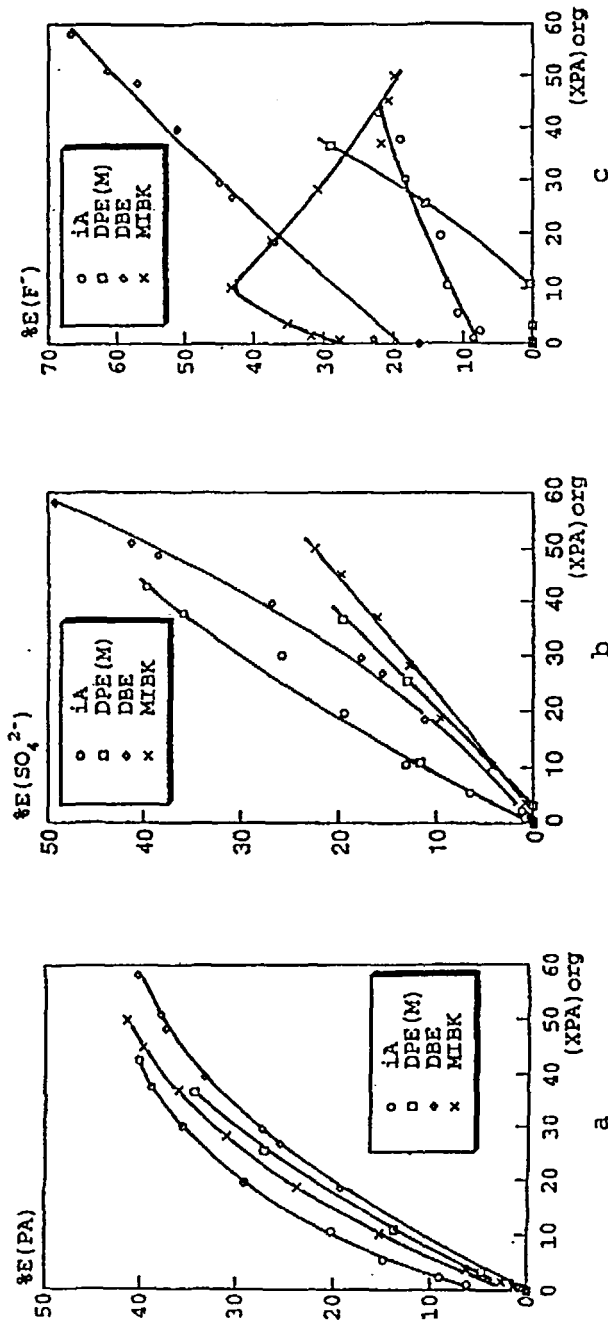FIG. 5   Extraction percent of PA, SO_4^{2-}, and F^- for different types of solvents.

TABLE 4
Dipole Moment μ and Water Solubility for the Different Solvents Considered

Solvents	iA	MIBK	DPE(M)	DBE
μ(D)	1.82 (21)	2.79 (22)	DPE: 1.32 (21) DIPE: 1.22 (21)	1.18 (21)
Water solubility (wt%) at 25°C	9.6 (8)	1.8 (7)	0.4 (9)	0.1 (10)

This assumption is confirmed by results obtained when using a mixture of PA and KH_2PO_4 whose total equals P_2O_5 (50%). Indeed, the distribution coefficient of P_2O_5 decreases when the amount of KH_2PO_4 in the mixture increases (Table 5).

Figures 5(b), 5(c), and 6 represent the percentage extracted of each impurity (MgO, Al_2O_3, Fe_2O_3, SO_4^{2-}, and F^-) as a function of PA concentration in the organic phase for MIBK and the other solvents considered above. All these solvents show the same behavior globally, extracting SO_4^{2-} and F^- to a higher extent than metallic impurities. This fact makes these solvents unsuitable for anionic impurity purification.

With regard to the specific behavior of each solvent, MIBK has the best selectivity against SO_4^{2-}. When considering metallic impurities, the selectivity of MIBK is always intermediate between those of iA and ethers. The solvent affinity for the metallic impurities follows the order

$$iA > MIBK > \text{ethers}$$

Thus, solvents which seem to be good extractants for PA show the same tendency for the cationic impurities [except in the case of DPE(M)]. Moreover, among the solvents considered, DBE has the best selectivity

TABLE 5
Effect of KH_2PO_4 Addition on the Distribution Coefficient of P_2O_5

Total P_2O_5 (wt%)	50	50	50	50	50	50
P_2O_5 introduced as KH_2PO_4 (wt%)	0	0.40	1.25	2.5	3.75	5.0
$D(P_2O_5) = \dfrac{X(P_2O_5)_{org}}{X(P_2O_5)_{aq}}$	0.52	0.47	0.40	0.35	0.32	0.27
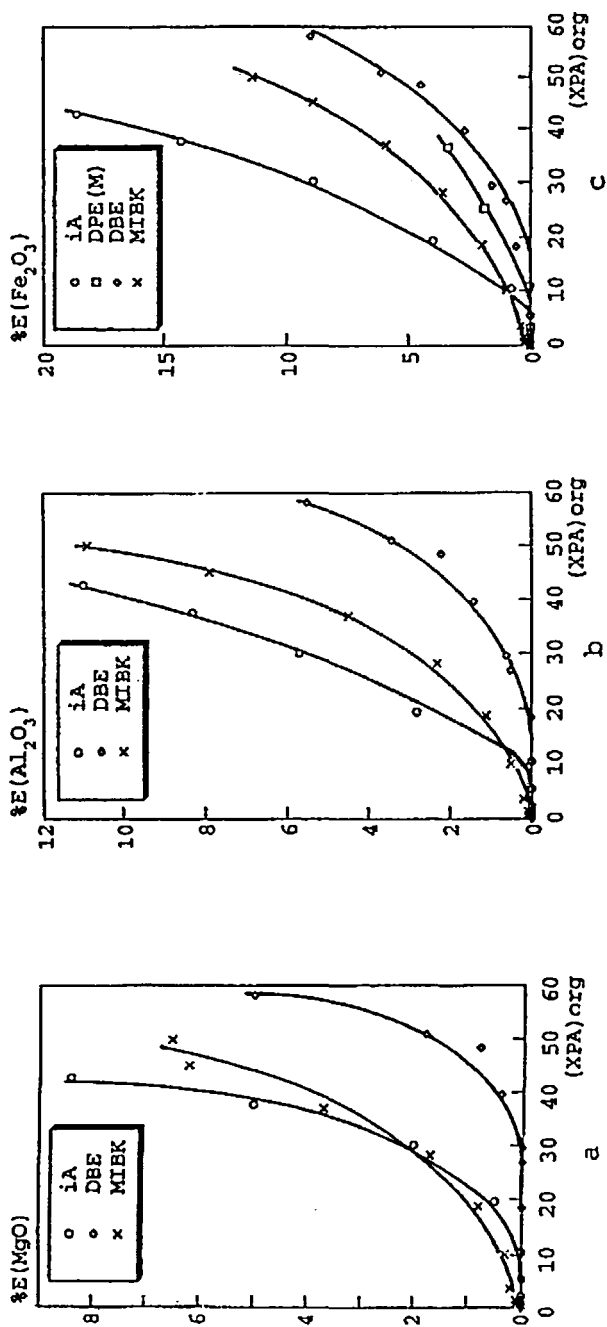
FIG. 6 Extraction percent of MgO, Al₂O₃, and Fe₂O₃ for different types of solvents.

against metallic impurities. Nevertheless, it extracts the lowest percentage of PA.

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